

We claim:

1. An organic, small pore area material comprising a monolithic aerogel, wherein its smallest dimension is greater than about 3 inches; and said aerogel is substantially free of cracks.

2. An organic, small pore area material comprising a monolithic aerogel prepared using a non-critical drying process, wherein its smallest dimension is greater than about 3 inches; and said aerogel is substantially free of cracks.

3. An organic, small pore area material comprising a monolithic aerogel prepared using a non-critical drying process, having a density less than about  $300 \text{ kg/m}^3$ , and wherein said aerogel is substantially free of cracks.

4. An organic, small pore area material comprising a monolithic aerogel prepared using a non-critical drying process, having a surface area less than about  $200 \text{ m}^2/\text{g}$ , and wherein said aerogel is substantially free of cracks.

5. An organic, small pore area material comprising a monolithic aerogel prepared using a non-critical drying process in which the material is substantially dried in less than about 24 hours, and wherein said aerogel is substantially free of cracks.

6. An organic, small pore area material comprising:

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(a) greater than about 80 % open pores;  
and

(b) a density less than about  $300 \text{ kg/m}^3$ .

7. The small pore area material according to any one of claims 1-5, wherein the aerogel shrinks less than about 25 % (by volume).

8. The small pore area material according to any one of claims 1-5, wherein the aerogel does not shrink substantially.

9. The small pore area material according to any one of claims 1-5, wherein the average pore area is less than about 200  $\mu\text{m}^2$ .

10. The small pore area material according to any one of claims 1-5, wherein the average pore area is less than about 100  $\mu\text{m}^2$ .

11. The small pore area material according to any one of claims 1-5, wherein the average pore area is less than about 50  $\mu\text{m}^2$ .

12. The small pore area material according to any one of claims 1-5, wherein the average pore area is less than about  $0.8 \mu\text{m}^2$ .

13. The small pore area material according to any one of claims 1-5, wherein the average pore area is less than about 2000  $\mu\text{m}^2$ .

14. An organic, small pore area material formed in situ having a monolithic form and a density of less than about 300 kg/m<sup>3</sup>.

15. An organic, small pore area material formed in situ having a monolithic form and a surface area of less than about  $200 \text{ m}^2/\text{g}$ .

16. An organic, small pore area material formed in situ in less than about 24 hours and having a monolithic form.

17. The small pore area material according to any one of claims 14-16, wherein the material comprises a monolithic aerogel.

18. The small pore area material according to any one of claims, 14-16 wherein the smallest dimension of the material is greater than about 3 inches.

19. The small pore area material according to any one of claims 14-16, wherein the material is prepared using a non-critical drying process.

20. The small pore area material according to any one of claims 14-16, wherein the material comprises:

- (a) greater than about 80 % open pores;
- and
- (b) a density less than about  $300 \text{ kg/m}^3$ .

21. The small pore area material according to any one of claim 1-5 or 14-16, wherein the density is less than about  $275 \text{ kg/m}^3$ .

22. The small pore area material according to claim 1-5 or 14-16, wherein the density is less than about  $250 \text{ kg/m}^3$ .

24. The small pore area material according to claim 1-5 or 14-16, wherein the density is less than about 100 kg/m<sup>3</sup>.

26. The small pore area material according to claim 20, wherein the thermal conductivity is less than about 0.008 W/(m·K) at a pressure of up to about 10 Torr.

28. The small pore area material according to claim 27, wherein the thermal conductivity is less than about 0.007 W/(m·K) at a pressure of up to about 1 Torr.

29. An organic, small pore area material having a monolithic form and a thermal conductivity less than about 0.005 W/(m·K) at a pressure of up to about 0.1 Torr, wherein said small pore area material is formed using a non-critical drying process.

30. The small pore area material according to claim 29, wherein the thermal conductivity is less than about  $0.0035 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 0.1 Torr.

31. The small pore area material according to any one of claims 1-5 or 14-16, wherein said small pore area material has a thermal conductivity less than about  $0.0135 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 10 Torr, and said material has a monolithic form and is formed using a non-critical drying process.

32. The small pore area material according to claim 31, wherein the thermal conductivity is less than about  $0.008 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 10 Torr.

33. The small pore area material according to any one of claims 1-5 or 14-16, wherein said small pore area material has a thermal conductivity less than about  $0.009 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 1 Torr, and said material has a monolithic form and is formed using a non-critical drying process.

34. The small pore area material according to claim 33, wherein the thermal conductivity is less than about  $0.007 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 1 Torr.

35. The small pore area material according to any one of claims 1-5 or 14-16, wherein said small pore area material has a thermal conductivity less than about  $0.005 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 0.1 Torr, and said material has a monolithic form and is formed using a non-critical drying process.

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36. The small pore area material according to claim 35, wherein the thermal conductivity is less than about 0.0035 W/(m·K) at a pressure of up to about 0.1 Torr.

37. A small pore area material comprising acetic acid.

38. The small pore area material according to any one of claims 1-5 or 14-16, comprising acetic acid.

39. A sol-gel polymerization process using acetic acid.

40. A small pore area material comprising a hydroxylated aromatic; a solvent capable of providing hydrogen bonding and/or covalent modifications within the small pore area material; and an electrophilic linking agent.

41. The small pore area material of claim 40, wherein the solvent comprises a hydrogen-bonding agent.

42. The small pore area material of claim 41, wherein said hydrogen-bonding agent comprises a carboxylic acid.

43. The small pore area material of claim 42, wherein said carboxylic acid is selected from the group consisting of acetic acid, formic acid, propionic acid, butyric acid, pentanoic acid, and isomers thereof.

44. The small pore area material of claim 43, wherein said carboxylic acid is acetic acid.

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45. The small pore area material of claim 40, wherein said hydroxylated aromatic is a hydroxylated benzene compound.

46. The small pore area material of claim 40, wherein said hydroxylated aromatic comprises a phenolic-novolac resin.

47. The small pore area material of claim 40, wherein said electrophilic linking agent comprises an aldehyde.

48. The small pore area material of claim 40, wherein said electrophilic linking agent comprises furfural.

49. The small pore area material of claim 40, wherein said electrophilic linking agent comprises alcohol.

50. The small pore area material of claim 49, wherein said alcohol is furfuryl alcohol.

51. The small pore area material of claim 40, wherein said small pore area material is prepared during a sol-gel polymerization process.

52. An organic, small pore area material produced in a method that uses a surfactant.

53. The small pore area material of any one of claims 1-5 or 14-16, wherein said material is produced in a method that uses a surfactant.

54. A method for preparing an organic, small pore area material, said method comprising the steps of:

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(a) forming a solution comprising a hydroxylated aromatic, an electrophilic linking agent, and a hydrogen-bonding agent;

(b) allowing said solution to form a sol-gel; and,

(c) removing substantially all of the fluid portion of said sol-gel.

55. The method of claim 54, wherein the solution formed in step (a) further comprises a catalyzing agent.

56. The method of claim 55, wherein said catalyzing agent is independently selected from the group consisting of hydrochloric acid, sulfuric acid and hydrobromic acid.

57. The method of claim 54, wherein step (b) includes the substep of subjecting said solution to either: (i) a temperature or a pressure higher than ambient; or (ii) a temperature and a pressure higher than ambient.

58. The method of claim 54, wherein step (c) includes the substep of evaporating said fluid portion at ambient conditions.

59. The method of claim 54, further including the substep of subjecting said fluid portion to either: (i) higher than ambient temperatures or lower than ambient pressures; or (ii) higher than ambient temperatures and lower than ambient pressures.

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60. The method of claim 54, wherein step (c) is substantially accomplished by subjecting said sol-gel to centrifugation.

61. The method of claim 54, wherein step (c) is substantially accomplished by subjecting said sol-gel to freeze drying.

62. The method of claim 54, wherein step (c) is substantially accomplished by subjecting said sol-gel to a gas pressure differential across said sol-gel.

63. The method of claim 54, wherein step (c) is substantially accomplished by supercritical extraction of said sol-gel.

64. The method of claim 54, further comprising the step (d) of pyrolyzing said low density microcellular material at a pyrolysis temperature to form a carbonized derivative of said low density microcellular material.

65. A method for preparing a low density microcellular material according to any one of claims 1-5, said method comprising the steps of:

- (a) forming a sol-gel; and
- (b) removing substantially all of the fluid portion of said sol-gel by non-supercritical extraction.

66. A method for preparing a small pore area material according to any one of claims 1-5, said method comprising the steps of:

- (a) forming a sol-gel; and

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(b) removing substantially all of the fluid portion of said sol-gel by non-supercritical extraction.

67. A composition of matter prepared by sol-gel polymerization using acetic acid.

68. A method for removing fluid from a sol-gel comprising the steps of:

- (a) forming a solution;
- (b) allowing said solution to form a sol-gel;
- (c) adding a low surface tension solvent to the sol-gel;
- (d) applying a pressure differential across the sol-gel;
- (e) removing substantially all of the original pore fluid portion of said sol-gel; and
- (f) removing the lower surface tension solvent.

69. A method for preparing an organic, low density microcellular material, said method comprising the steps of:

- (a) forming a solution;
- (b) allowing said solution to form a sol-gel;
- (c) adding a low surface tension solvent to the sol-gel;
- (d) applying a pressure differential across the sol-gel;
- (e) removing substantially all of the original pore fluid portion of said sol-gel; and

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(f) removing the lower surface tension solvent .

70. A method for preparing an organic, low density microcellular material, said method comprising the steps of:

- (a) forming a solution comprising a hydroxylated aromatic, an electrophilic linking agent, and a hydrogen-bonding agent;
- (b) allowing said solution to form a sol-gel;
- (c) adding a low surface tension solvent to the sol-gel;
- (d) applying a pressure differential across the sol-gel;
- (e) removing substantially all of the original pore fluid portion of said sol-gel, and
- (f) removing the low surface tension solvent

71. A method for preparing an organic, small pore area material, said method comprising the steps of:

- (a) forming a solution;
- (b) allowing said solution to form a sol-gel;
- (c) adding a lower surface tension solvent to the sol-gel;
- (d) applying a pressure differential across the sol-gel;
- (e) removing substantially all of the original pore fluid portion of said sol-gel, and
- (f) removing the lower surface tension solvent

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72. A method for preparing an organic, small pore area material, said method comprising the steps of:

- (a) forming a solution comprising a hydroxylated aromatic, an electrophilic linking agent, and a hydrogen-bonding agent;
- (b) allowing said solution to form a sol-gel;
- (c) adding a low surface tension solvent to the sol-gel;
- (d) applying a pressure differential across the sol-gel;
- (e) removing substantially all of the original pore fluid portion of said sol-gel, and
- (f) removing the low surface tension solvent

73. The method according to any one of claims 68-72, wherein said low surface tension solvent is an organic solvents with surface tension lower than that of the solvent used in preparing the sol-gel. .

74. The method according to any one of claims 68-72, wherein said lower surface tension solvent is selected from the group consisting of hexane, ethyl ether, pentane, isopentane, acetone, methanol, ethanol or isopropanol.

75. The method according to any one of claims 68-72, wherein said low surface tension solvent comprises a hexane compound.

76. The method of claim 70 or 72, wherein said hydroxylated aromatic comprises a hydroxylated benzene compound.

77. The method of claim 70 or 72, wherein said hydroxylated aromatic comprises a phenolic novolak compound.

78. The method according to any one of claims 63-67, wherein said low surface tension solvent is removed by evaporation, freeze drying or centrifugation

79. The method of claim 70 or 72, wherein said electrophilic linking agent comprises an aldehyde.

80. The method of claim 70 or 72, wherein said electrophilic linking agent comprises furfural.

81. The method of claim 70 or 72, wherein said hydrogen-bonding agent comprises a carboxylic acid.

82. The method of claim 70 or 72, wherein said hydrogen-bonding agent comprises acetic acid, formic acid, propionic acid, butyric acid, pentanoic acid or an isomer thereof.

83. The method of claim 70 or 72, wherein said hydrogen-bonding agent comprises acetic acid.

84. A carbonized form of the low density microcellular material according to any one of claims 1-5.

85. A carbonized form of the small pore area material according to any one of claims 1-5.

86. A low density microcellular material that is black without the use of an opacifier.

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87. A small pore area material that is black without the use of an opacifier.

88. An organic small pore area material with an average pore area of about 2000 to about 50  $\mu\text{m}^2$ .

89. An organic small pore area material formed by a sol-gel polymerization process.

90. The small pore area material according to claim 6, wherein said material is a low density microcellular material.

91. The small pore area material according to claim 14, wherein said material is a low density microcellular material.

92. The small pore area material according to claim 15, wherein said material is a low density microcellular material.

93. The small pore area material according to claim 16, wherein said material is a low density microcellular material.

94. The low density microcellular material according to any one of claims 90-92, wherein the smallest dimension of the material is greater than about 3 inches.

95. The low density microcellular material according to any one of claims 90-92, wherein the material is prepared using a non-critical drying process.

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96. The low density microcellular material according to any one of claims 90-92, wherein the material comprises:

- (a) greater than about 80 % open pores;
- (b) a density less than about  $300 \text{ kg/m}^3$ .

97. The low density microcellular material according to any one of claims 90-92, wherein the density is less than about  $275 \text{ kg/m}^3$ .

98. The low density microcellular material according to claims 90-92, wherein the density is less than about  $250 \text{ kg/m}^3$ .

99. The low density microcellular material according to claims 90-92, wherein the density is less than about  $150 \text{ kg/m}^3$ .

100. The low density microcellular material according to claims 90-92, wherein the density is less than about  $100 \text{ kg/m}^3$ .

101. The small pore area material according to claim 25, wherein said material is a low density microcellular material.

102. The low density microcellular material according to claim 101, wherein the thermal conductivity is less than about  $0.008 \text{ W/(m}\cdot\text{K)}$  at a pressure of up to about 10 Torr.

103. The small pore area material according to claim 27, wherein said material is a low density microcellular material.

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is less than about 0.007 W/(m•K) at a pressure of up to about 1 Torr.

111. The low density microcellular material according to any one of claims 90-92, wherein said low density microcellular material has a thermal conductivity less than about 0.005 W/(m•K) at a pressure of up to about 0.1 Torr, and said material has a monolithic form and is formed using a non-critical drying process.

112. The low density microcellular material according to claim 111, wherein the thermal conductivity is less than about 0.0035 W/(m•K) at a pressure of up to about 0.1 Torr.

113. A low density microcellular material comprising acetic acid.

114. The low density microcellular material according to any one of claims 90-92, comprising acetic acid.

115. A low density microcellular material comprising a hydroxylated aromatic; a solvent capable of providing hydrogen bonding and/or covalent modifications within the low density microcellular material; and an electrophilic linking agent.

116. The low density microcellular material of claim 115, wherein the solvent comprises a hydrogen-bonding agent.

117. The low density microcellular material of claim 116, wherein said hydrogen-bonding agent comprises a carboxylic acid.

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118. The low density microcellular material of claim 117, wherein said carboxylic acid is selected from the group consisting of acetic acid, formic acid, propionic acid, butyric acid, pentanoic acid, and isomers thereof.

119. The low density microcellular material of claim 117, wherein said carboxylic acid is acetic acid.

120. The low density microcellular material of claim 115, wherein said hydroxylated aromatic is a hydroxylated benzene compound.

121. The low density microcellular material of claim 115, wherein said hydroxylated aromatic comprises a phenolic-novolak resin.

122. The low density microcellular material of claim 115, wherein said electrophilic linking agent comprises an aldehyde.

123. The low density microcellular material of claim 115, wherein said electrophilic linking agent comprises furfural.

124. The low density microcellular material of claim 115, wherein said electrophilic linking agent comprises alcohol.

125. The low density microcellular material of claim 124, wherein said alcohol is furfuryl alcohol.

126. The low density microcellular material of claim 115, wherein said low density microcellular material is in the form of a complex prepared during a sol-gel polymerization process.

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127. An organic, low density microcellular material produced in a method that uses a surfactant.

128. The low density microcellular material of any one of claims 90-92, wherein said material is produced in a method that uses a surfactant.

129. A method for preparing an organic, low density microcellular material, said method comprising the steps of:

- (a) forming a solution comprising a hydroxylated aromatic, an electrophilic linking agent, and a hydrogen-bonding agent;
- (b) allowing said solution to form a sol-gel; and,
- (c) removing substantially all of the fluid portion of said sol-gel.

130. The method of claim 129, wherein the solution formed in step (a) further comprises a catalyzing agent.

131. The method of claim 130, wherein said catalyzing agent is independently selected from the group consisting of hydrochloric acid, sulfuric acid and hydrobromic acid.

132. The method of claim 129, wherein step (b) includes the substep of subjecting said solution to either: (i) a temperature or a pressure higher than ambient; or (ii) a temperature and a pressure higher than ambient.

133. The method of claim 129, wherein step (c) includes the substep of evaporating said fluid portion at ambient conditions.

134. The method of claim 129, further including the substep of subjecting said fluid portion to either: (i) higher than ambient temperatures or lower than ambient pressures; or (ii) higher than ambient temperatures and lower than ambient pressures.

135. The method of claim 129, wherein step (c) is substantially accomplished by subjecting said sol-gel to centrifugation.

136. The method of claim 129, wherein step (c) is substantially accomplished by subjecting said sol-gel to freeze drying.

137. The method of claim 129, wherein step (c) is substantially accomplished by subjecting said sol-gel to a gas pressure differential across said sol-gel.

138. The method of claim 129, wherein step (c) is substantially accomplished by supercritical extraction of said sol-gel.

139. The method of claim 129, further comprising the step (d) of pyrolyzing said low density microcellular material at a pyrolysis temperature to form a carbonized derivative of said low density microcellular material.

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